STEROIDAL SAPOGENINS. XXXI. GENTROGENIN AND CORRELLOGENIN, NEW SAPOGENINS FROM *Dioscorea spiculiflora*[1]

Sir:

Some years ago Marker announced the isolation of botogenin and neobotogenin from *D. mexicana*.[2a,b] The structures assigned had both a 12-keto and a 5,6 double bond. Since substances with these groupings would be particularly desirable as cortisone precursors, there was an extensive but fruitless search made for them. We have now found in several collections of *D. spiculiflora* two isomers which have the structures assigned to botogenin and neobotogenin. Since, however, their melting points and those of their acetates differ greatly from Marker's compounds (Table I) and, since the latter were inadequately characterized, we wish to rename these sapogenins and propose *gentrogenin* (I) and *correllogenin* (II) for them.[3,4] Because of their possible chemical importance, we wish to make a preliminary announcement of their occurrence and structure proof.

TABLE I

	M.p., °C.	
	Sapogenin	Acetate
Botogenin	262	248
Neobotogenin	246–248	234
Gentrogenin	215–216	227
Correllogenin	209–211	213–214

Treatment of the crude sapogenin mixture with Girard's reagent gave a mixture of I and II from which the less soluble I acetate was readily crystallized, (m.p. 227°, $[\alpha]^{25}D$ −56° ($CHCl_3$); calcd. for $C_{29}H_{42}O_5$: C, 74.01; H, 9.00; found: C, 74.10; H, 9.10), which on hydrolysis gave I (m.p. 215–216°, $[\alpha]^{25}D$ −57°; calcd. for $C_{27}H_{40}O_4$: C, 75.66; H, 9.41; found: C, 75.46; H, 9.51). The infrared spectrum of I showed a strong carbonyl peak at 1712 cm.$^{-1}$, a weak band at 836 cm.$^{-1}$ associated with a Δ^5-ethylenic band,[5a,b] and the typical "22a" (= 25D) fingerprint spectrum 980(S), 919(W), 898(S), 863(W) cm.$^{-1}$.[6a,b]

Catalytic reduction of I acetate followed by oxidation with CrO_3–acetic acid gave hecogenin acetate, m.p. 245–247°, infrared spectrum identical to an authentic specimen; Wolff–Kishner reduction of I acetate gave diosgenin, m.p. 204–206°, infrared spectrum identical with an authentic sample. These reactions establish the structure of gentrogenin as 5-20a,22α,25D-spirostene-3β-ol-12-one.[7]

Repeated fractional crystallization of soluble mother liquors gave II acetate, (m.p. 213–214°, $[\alpha]^{25}D$ −60°, calcd. for $C_{29}H_{42}O_5$: C, 74.01; H, 9.00; found: C, 74.10; H, 9.10); infrared spectrum showed two strong bands at 1737, 1713 cm.$^{-1}$ (acetate and 12 carbonyl, respectively), a weak 838 cm.$^{-1}$ band[5a,b] and typical "22b" (= 25 L) bands[6a,b] at 986(S), 920(S), 897(W), and 852(W) cm.$^{-1}$. Catalytic reduction of II acetate followed by mild CrO_3–acetic acid oxidation gave a compound which, from the method of preparation and infrared,[8] we deduce to be 5a-20α,22a,25L-spirostan-3β-ol-12-one 3-acetate, m.p. 214–216°, $[\alpha]^{25}D$ −12°. Infrared shows 1733, 1708 cm.$^{-1}$ carbonyl bands, typical "22b" (= 25L) fingerprint spectrum, and absence of ethylenic 838 cm.$^{-1}$ absorption. Hydrolysis of II acetate gave II, (m.p. 209–211°, $[\alpha]^{25}D$ −69°, calcd. for $C_{27}H_{40}O_4$: C, 75.66; H, 9.41; found: C, 75.14; H, 9.63). Wolff–Kishner reduction of II gave the known yamogenin m.p. 190–194°, infrared essentially identical to an authentic sample. The above reactions establish the structure of correllogenin as 5-20α,22a,25L-spirostene-3β-ol-12-one.

Gentrogenin and correllogenin have been found only in tubers of *Dioscorea spiculiflora*, which occurs in southern Mexico. They are always present in a mixture with diosgenin and yamogenin and constitute 15–25% of the total sapogenin content which averages about 3% on a dry basis.

We wish to thank C. R. Eddy and C. S. Fenske for the infrared spectra, K. M. Zbinden for the C and H analyses, and R. F. Mininger for the optical rotations.

(1) Paper XXX: M. E. Wall, submitted in *Experientia*, 11, 340, (1955).

(2) (a) R. E. Marker and J. Lopez, THIS JOURNAL, **69**, 2397 (1947), (b) R. E. Marker, *ibid.*, **71**, 2656 (1949).

(3) In honor of Doctors H. S. Gentry and D. S. Correll, Horticultural Crops Research Branch, Agricultural Research Service, United States Department of Agriculture, Beltsville, Maryland, who obtained the plant material from which these new sapogenins were isolated.

(4) For precedents for renaming several sapogenins first allegedly isolated by Marker, *cf.* THIS JOURNAL, **75**, 4437 (1953); *J. Chem. Soc.*, 1671 (1955).

(5) (a) R. N. Jones, P. Humphries, F. Herling and K. Dobriner, THIS JOURNAL, **73**, 3215 (1951); (b) C. R. Eddy, M. E. Wall, M. K. Scott, *Anal. Chem.*, **25**, 266 (1953).

(6) (a) M. E. Wall, C. R. Eddy, M. L. McClennan, and M. E. Klumpp, *Anal. Chem.*, **24**, 1337 (1952); (b) R. N. Jones, E. Katzenellenbogen and K. Dobriner, THIS JOURNAL, **75**, 158 (1953).

(7) For present concepts of the stereochemistry of the sapogenin side chain *cf.* I. Scheer, R. B. Kostic and E. Mosettig, THIS JOURNAL, **77**, 641 (1955); J. B. Ziegler, W. E. Rosen and A. C. Shabica, *ibid.*, **77**, 1223 (1955); M. E. Wall, S. Serota and C. R. Eddy, *ibid.*, **77**, 1230 (1955); and M. E. Wall, ref. 1. It seems that natural sapogenins do not differ at C_{22}.

(8) Insufficient material was available for carbon and hydrogen analyses.